

NASA TECHNICAL NOTE



NASA TN D-2823

NASA TN D-2823

N65-23693

FACILITY FORM 602

(ACCESSION NUMBER)

(PAGES)

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# EFFECT OF THREE METAL ADDITIONS ON GRAIN SIZE OF MAGNESIUM OXIDE AFTER HIGH-TEMPERATURE HEAT TREATMENTS\*

by Alan Arias

Lewis Research Center

## SUMMARY

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The effects of additions of chromium, molybdenum, and tungsten on the grain growth of vacuum hot-pressed magnesium oxide were investigated. The effects of heat-treating temperature, time, and hydrogen cleaning of the specimens before hot-pressing were also investigated.

The effects of additions of tungsten, molybdenum, and chromium depend on the amount of addition, and, for tungsten, also on the heat-treating temperature. In general, beyond about 4-volume-percent addition, all three metals inhibit the grain growth of magnesium oxide at 1620<sup>0</sup> C. The effectiveness of these metals as grain-growth inhibitors for magnesium oxide at 1620<sup>0</sup> C decreases in the order: chromium, molybdenum, tungsten.

Magnesium oxide with chromium, molybdenum, and tungsten additions shows a decrease (compared with pure magnesium oxide) in the rate of grain growth, as predicted by theory. The effect of amount of tungsten addition on the temperature dependence of grain growth of magnesium oxide was as predicted (at least qualitatively) by theory.

It is surmised that the observed grain-growth dependence on composition, amount of addition, temperature, and time is due to the combined effects of dissolved impurities and the grain-growth-inhibiting properties of the metal additions that act as inclusions.

## INTRODUCTION

AUTHOR ↑

In a previous investigation (ref. 1) on the effects of metals and compound additions on the grain growth of oxides, it was shown that although most of the metals and compounds tried are effective grain-growth inhibitors, a few of them actually enhance grain growth. This grain-growth enhancement appears to be caused by impurities from the

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\*The material contained in this report was submitted as part of a thesis to Case Institute of Technology, June 1964, in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

addition or by diffusion of the addition in the matrix oxide and is temperature dependent.

The effects of temperature and time at temperature (ref. 2) as well as the effects of inclusions (refs. 2 and 3) on the grain growth of metals and alloys are well known. Although the general validity of the theory for the effects of inclusions on grain growth appears to hold for metals and alloys (ref. 2), the validity of the theory has not been established experimentally in the case of ceramics. Furthermore, only a very few works (refs. 1 and 4) on the effects of metal additions on the grain growth of oxides has been published. It is for this reason that the present investigation on the effects of amount of metal addition, temperature, and time at temperature on the grain growth of an oxide was undertaken.

In this investigation, the effects of the amount of metal addition of tungsten (W), molybdenum (Mo), and chromium (Cr) on the grain growth of magnesium oxide (MgO) were studied as a function of heat-treating time and for W additions also as a function of temperature. Some experiments on diffusion, effect of oxide additions, and hot-pressing in reducing atmospheres were carried out in an attempt to clarify some of the grain-growth phenomena encountered in the course of the investigation.

## MATERIALS AND EXPERIMENTAL PROCEDURES

The raw materials used in the present investigation were the powders of magnesium oxide (MgO), tungsten oxide ( $\text{WO}_3$ ), molybdenum oxide ( $\text{MoO}_3$ ), chromium oxide ( $\text{Cr}_2\text{O}_3$ ), W, Mo, and Cr. The particle sizes, manufacturer's analysis, treatment, and sources of the various materials used are given in table I.

TABLE I. - SOURCE, COMPOSITION, TREATMENT, AND PARTICLE SIZE OF RAW MATERIALS

Material	Supplier (a)	Composition, percent	Milling time, hr	Average particle size, $\mu$	Method
Chromium	A	99 Chromium min.	48	0.52	BET <sup>b</sup>
Molybdenum	B	99.9 Molybdenum, 0.1 oxygen	48	.19	BET
Tungsten	B	99.9 Tungsten, 0.13 oxygen	2	.24	BET
Chromium oxide	C	99.8 Chromium oxide min.	0	----	----
Magnesium oxide	C	98.5 Magnesium oxide, 0.5 sodium	0	.46	BET
Molybdenum oxide	D	99.5 Molybdenum oxide min.	0	----	----
Tungsten oxide	E	99.9 Tungsten oxide	0	----	----

<sup>a</sup>Qualified requesters may obtain a key to this column.

<sup>b</sup>Determination of surface area by adsorption of gas.

Three of the as-received metal powders were milled for the times indicated in table I to break up agglomerates or to bring their particle sizes in line with those of other metals with which they were to be compared and to allow densification at low hot-pressing temperatures. All milling was carried out in 2-liter-capacity, tungsten carbide mills with 4.3 kilograms of tungsten carbide balls and 1 liter of acetone as the grinding medium. All milling was carried out at 80 rpm.

After completion of milling, the powder-acetone slurry was dried in a stream of warm air, and the dried powders were passed through a 100-mesh sieve and stored in a vacuum desiccator.

The particle sizes of the MgO and metal additions were determined by a surface area technique using the BET method (ref. 5). The particle sizes determined by the BET method are based on the assumption that the particles are spherical. These average particle sizes are included in table I.

The following general procedure was observed in preparing the test specimens of the various compositions (ranging from 0 to 16-volume-percent metal addition). The MgO and the addition (calculated to give a fixed volume percent) were weighed, wet-mixed, dried, cold-pressed at 3000 pounds per square inch, and then vacuum-hot-pressed (with the equipment described in ref. 6) at  $1225^{\circ} \pm 25^{\circ}$  C and 2500 pounds per square inch for 1 hour to obtain a relatively dense compact of small grain size. These specimens are designated as "vacuum-hot-pressed." In some cases, the green compacts were treated in purified hydrogen at  $925^{\circ}$  C for 30 minutes under a 500-pound force before hot-pressing. This "hydrogen cleaning" was carried out in order to reduce oxide impurities in the metallic powders, since it is known that oxides may influence the grain growth of MgO and other oxides (refs. 7 and 8). Thermodynamic considerations indicate that the oxides of W, Mo, and Cr can be reduced by hydrogen under the conditions used in this investigation, provided that the partial pressure of water in the gas is sufficiently low - of the order of  $10^{-4}$  atmosphere for  $\text{Cr}_2\text{O}_3$ , the most difficult oxide to reduce as computed from available data (ref. 9). The specimens obtained by this procedure are designated as "hydrogen-cleaned and hot-pressed."

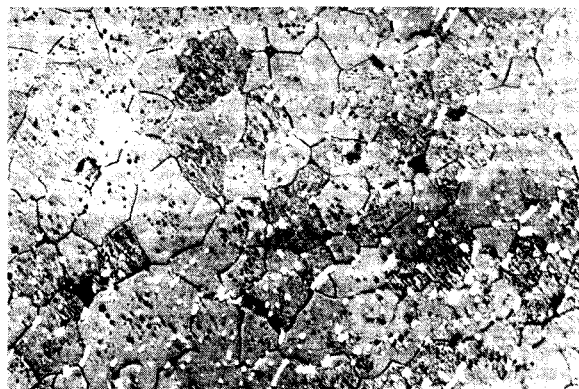
The processed compacts were surface ground to a depth of 0.040 inch on all faces to remove possible contamination by graphite or reaction products from the hot-pressing operation. The specimens were then cut into smaller test pieces and vacuum-heat-treated at temperatures higher than those used for hot-pressing ( $1400^{\circ}$  to  $1620^{\circ}$  C) to promote grain growth. The details of the various procedures used are given in reference 1. The cross section of each heat-treated specimen was polished, etched, and photomicrographed for grain-size determination.

The grain sizes of the hot-pressed and heat-treated specimens were measured in the following manner. The specimens were mounted in thermosetting plastic and were polished and etched by standard ceramographic techniques (ref. 10). Photomicrographs

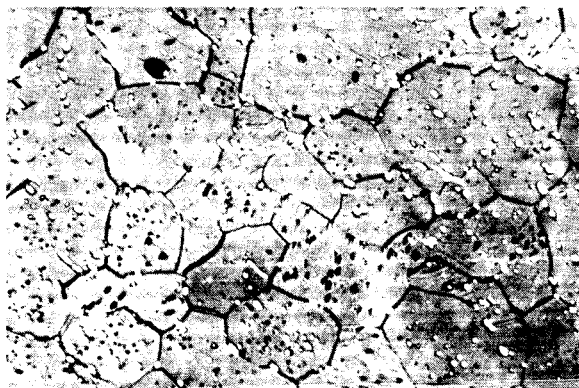
for grain-size determination were taken with a metallograph at linear magnifications between 50 and 1000, depending on the grain sizes involved.

The grain size was determined by lineal analysis (refs. 11 and 12). The "grain size" contribution of second-phase particles was corrected for by subtracting the (calculated) length of line falling on second-phase particles from the total length of the lines. Since the volume fraction of a second phase is equal to the area fraction in a plane through the sample and is also equal to the linear fraction of the second phase intercepting a random line in this plane (ref. 11), it follows that the presence of the second phase can be corrected for by multiplying the uncorrected "average intercept grain size" by the volume fraction of the continuous phase. Since the purpose of this investigation is to compare the relative effects of the various additions, only the average intercept grain size as defined is used here.

In the determination of grain sizes, usually upwards of 80 intersections were counted, giving a standard deviation of less than 7 percent (ref. 12). This number of intersections was readily obtainable at moderate magnifications in most of the specimens examined. Some of the specimens were two-layered structures, and in determining the grain size at the interface, usually only one line parallel to the interface could be traced because the grain-growth effects at the interface decrease rapidly with distance from it. Since fewer intersections were counted at the interface, the results have a standard deviation usually no better than 17 percent.



(a) 1 Hour at temperature.



(b) 4 Hours at temperature.



(c) 8 Hours at temperature.

Figure 1. - Effect of heat-treating time on grain size of magnesium oxide with 4-volume-percent molybdenum vacuum-heat-treated at 1620° C. X250.

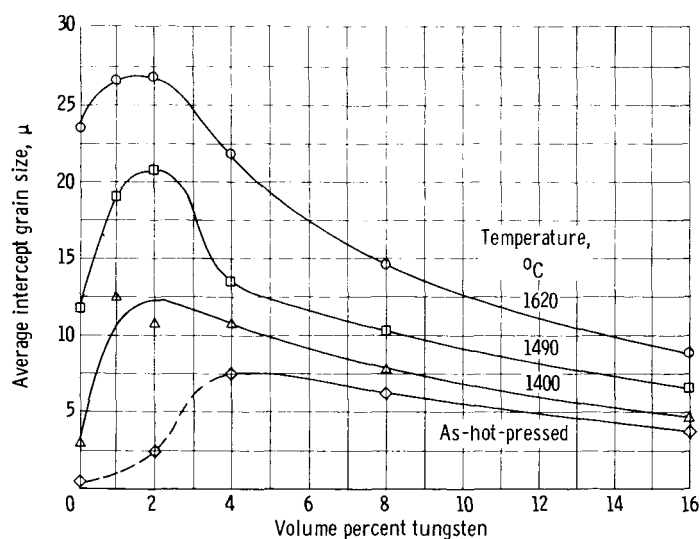


Figure 2. - Effect of amount of tungsten addition and temperature on grain size of magnesium oxide. All compositions were vacuum-hot-pressed at 1225° C and 2500 pounds per square inch for 1 hour followed by heat-treating at temperature indicated for 1 hour.

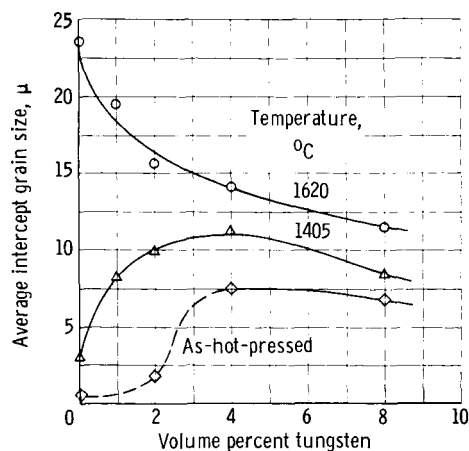


Figure 3. - Effect of amount of tungsten addition and temperature on grain size of hydrogen-cleaned magnesium oxide - tungsten cermets. All compositions were cleaned in purified hydrogen at 900° C for 30 minutes before hot-pressing at 1225° C and 2500 pounds per square inch for 1 hour followed by heat-treating in vacuum for 1 hour at temperature indicated.

## RESULTS

The color of the specimens varied from white for pure MgO to nearly black for some of the magnesia-metal compositions. The fact that hot-pressed pure MgO was white indicated no appreciable reduction by carbon. The as-hot-pressed density of the MgO matrix (corrected for the amount of metal addition) was 93 percent of the theoretical density with no significant difference between the various mixtures. Typical microstructures of as-heat-treated specimens are shown in figure 1. The white particles are metal; the small dark areas are either pores or pull outs; the gray background is MgO.

The effects of the amount of W and heat-treating temperature on the grain size of vacuum-hot-pressed MgO are shown in figure 2. The grain size of the as-hot-pressed specimens at low W levels was difficult to measure because of small grain size. For this reason, the corresponding curve is shown as a dashed line. The curves for isothermal grain size plotted against volume percent addition show maximums at about 2-volume-percent metal beyond which point the grain size decreases with increasing W percentage at all temperatures.

The effect of the amount of W addition and heat-treating temperature on the grain size of hydrogen-cleaned and hot-pressed specimens is shown in figure 3. Because of the hydrogen treatment, the maximums in the curves for grain size plotted against volume percent W are shifted to a higher volume percent (about 4) and occur only at the lower temperatures. Beyond these maximums, the grain size decreases with in-

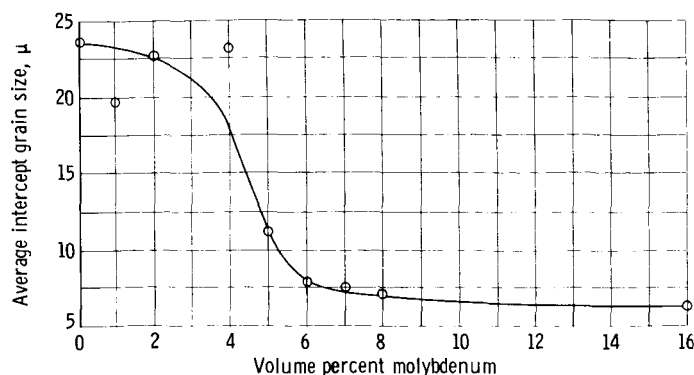


Figure 4. - Effect of molybdenum addition on grain size of magnesium oxide vacuum-heat-treated at  $1620^{\circ}\text{C}$  for 1 hour. All compositions were cleaned in purified hydrogen at  $900^{\circ}\text{C}$  for 30 minutes before hot-pressing at  $1225^{\circ}\text{C}$  and 2500 pounds per square inch for 1 hour, followed by vacuum-heat-treating at  $1620^{\circ}\text{C}$  for 1 hour.

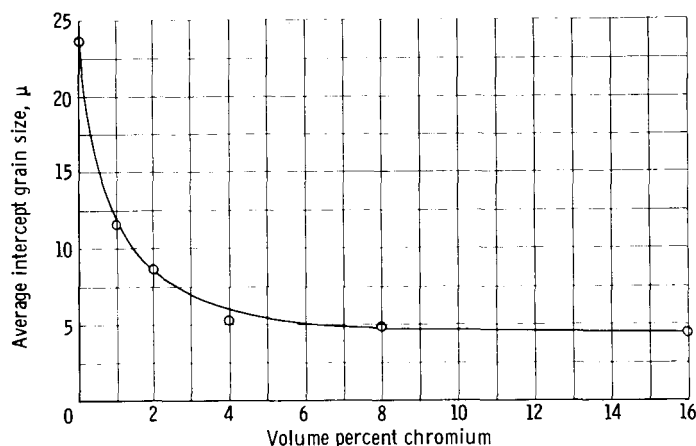


Figure 5. - Effect of amount of chromium addition on grain size of magnesium oxide after vacuum-heat-treating at  $1620^{\circ}\text{C}$  for 1 hour. All compositions were cleaned in purified hydrogen at  $900^{\circ}\text{C}$  for 30 minutes before hot-pressing at  $1225^{\circ}\text{C}$  and 2500 pounds per square inch for 1 hour, followed by vacuum-heat-treating at  $1620^{\circ}\text{C}$  for 1 hour.

creasing volume percent W at all temperatures.

The effects of the amount of Mo addition on the grain size of hydrogen-cleaned and hot-pressed MgO after heat-treating at  $1620^{\circ}\text{C}$  for 1 hour in vacuum are shown in figure 4. Up to about 4-volume-percent Mo, the grain size is practically independent of the amount of addition. Beyond 4 volume percent, the grain size decreases with increasing percent addition.

The effects of the amount of Cr addition on the grain size of hydrogen-cleaned and hot-pressed MgO after heat-treating at  $1620^{\circ}\text{C}$  for 1 hour in vacuum are shown in figure 5. This curve shows no inversion, and the grain size decreases with increasing volume percent Cr.

The data points from figures 2 and 3 have been replotted in figure 6 to show the effects of heat-treating temperature on the grain growth of MgO with W additions. The hydrogen-cleaned and hot-pressed specimens show a smaller temperature dependence of grain growth than do the specimens that were not hydrogen-cleaned.

The effects of heat-treating time on the grain growth of MgO with W, Mo, and Cr additions vacuum-heat-treated at  $1620^{\circ}\text{C}$  are shown in figure 7. All the specimens used in this part of the investigation were of the hydrogen-cleaned and hot-pressed variety. For a given kind of addition, the growth rate appears to be fairly insensitive to the amount of metal addition beyond about 4 volume percent.

A possible explanation for the "interface effect" discussed in reference 1 and the maximums in some of the curves for grain size against compositions shown in figures 2 and 3 is that either the metal addition, or oxides of this metal incompletely reduced by the hydrogen treatment, diffused into the MgO thereby accelerating its grain growth. To clarify this point, two additional series of experiments were carried out.



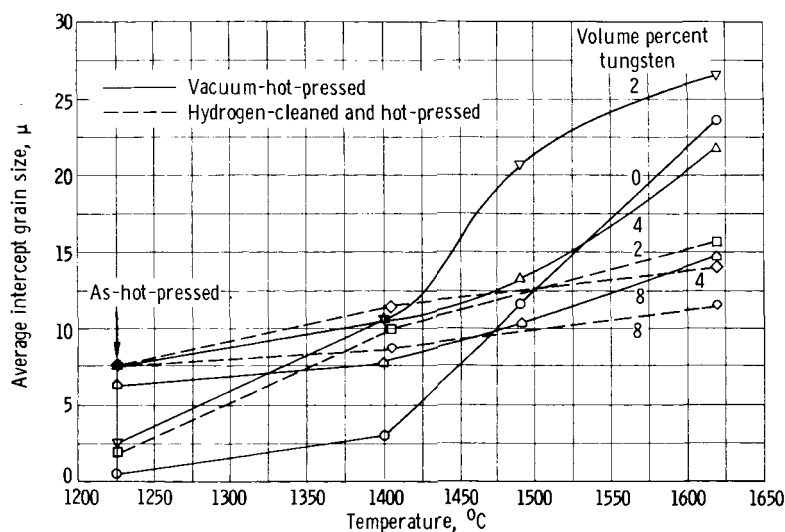
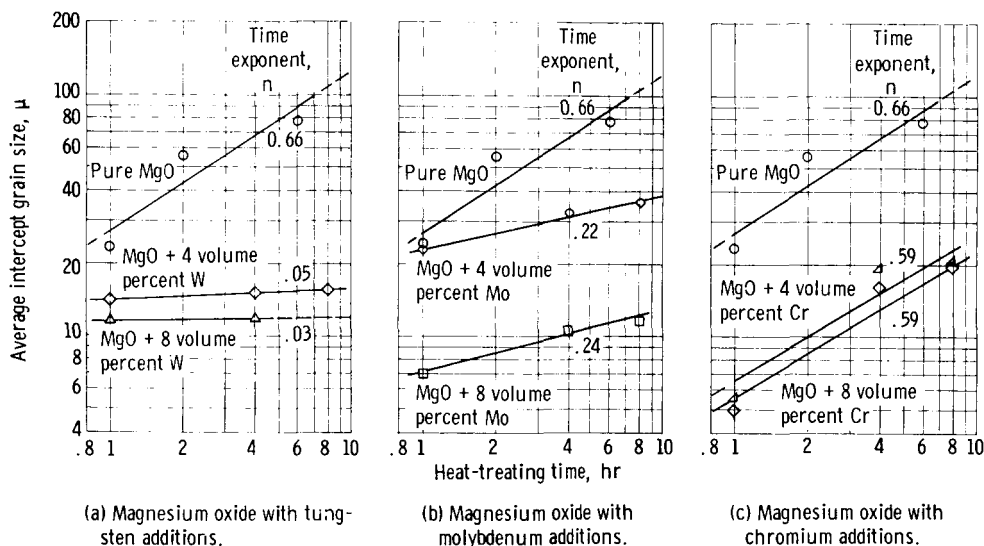


Figure 6. - Effect of heat-treating temperature on grain size of magnesium oxide with tungsten addition. All compositions were heat-treated for 1 hour at temperature indicated, except as noted.



(a) Magnesium oxide with tungsten additions.

(b) Magnesium oxide with molybdenum additions.

(c) Magnesium oxide with chromium additions.

Figure 7. - Effect of heat-treating time on grain size and time exponent  $n$  in equation  $D = Kt^n$  for magnesium oxide with metal additions. All compositions were hydrogen-cleaned and hot-pressed followed by heat-treating at  $1620^\circ\text{C}$  in vacuum.

The first series of experiments was performed to determine the effects of the oxides of W, Mo, and Cr on the grain growth of MgO. Specimens of MgO with 3.76, 4.13, and 6.49 weight percent of  $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$ , and  $\text{WO}_3$ , respectively, were prepared by vacuum-hot-pressing the mixtures at  $1225^\circ\text{C} \pm 25^\circ\text{C}$  at 2500 pounds per square inch for 1 hour. The weight percent oxide additions in these compositions correspond to approximately 1 volume percent of the respective metals. Each of these specimens was hot-pressed with a layer of the pure MgO bonded to it to compare grain-growth effects in the mixture with those in the bulk of the pure oxide and at the interface between the two layers.

TABLE II. - EFFECT OF OXIDE ADDITIONS ON  
GRAIN SIZE OF MAGNESIUM OXIDE

[All compositions were vacuum hot-pressed at 1225° C, at 2500 psi, for 1 hr followed by vacuum-heat-treating at 1620° C for 1 hr. The grain size of pure MgO after the same heat treatment was 23.5 $\mu$ .]

Oxide addition, weight percent	Average intercept grain size in mixture, $\mu$	Average intercept grain size in pure magnesium oxide at interface, $\mu$
3.76 Chromium oxide	25	70
4.13 Molybdenum oxide	36	91
6.49 Tungsten oxide	43	76

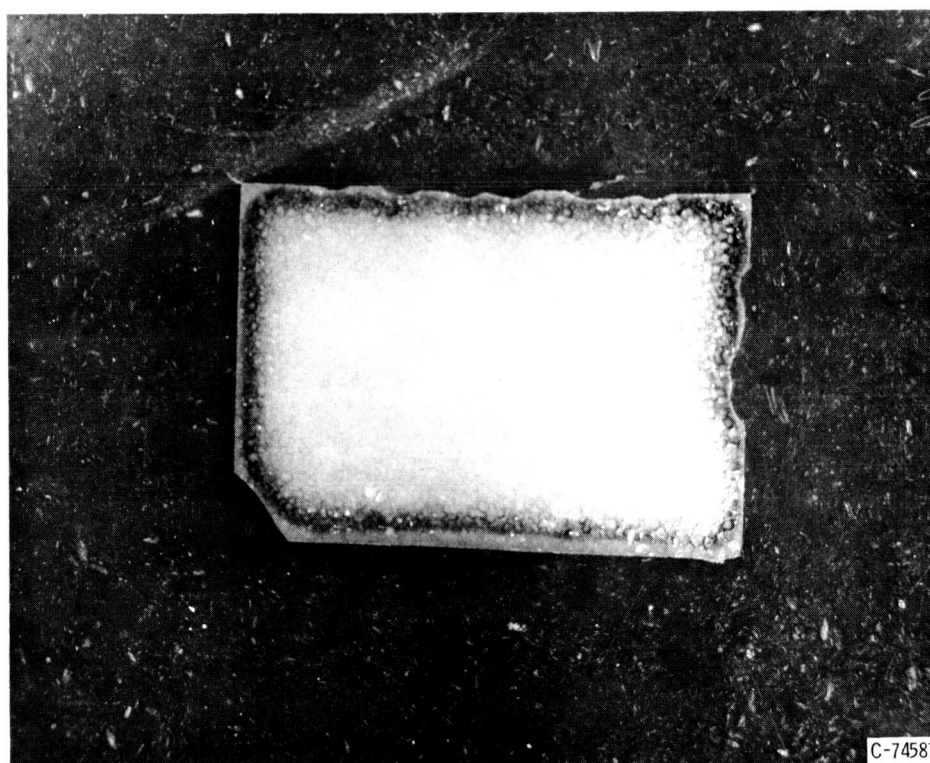


Figure 8. - Cross section of magnesium oxide specimen after vacuum-heat-treating at 1605° C for 16 hours with one surface (bottom edge of specimen) in contact with flat piece of chromium. X6.6.

Surface-ground specimens of each of these compositions were then vacuum-heat-treated at  $1620^{\circ}\pm 25^{\circ}$  C for 1 hour.

An undetermined amount of  $\text{MoO}_3$  and  $\text{WO}_3$  volatilized from the compacts during hot-pressing, so that the actual amounts of these oxides in the corresponding compacts is less than that corresponding to 1 volume percent of the metal.

The grain sizes of specimens of  $\text{MgO}$  with additions of  $\text{WO}_3$ ,  $\text{MoO}_3$ , and  $\text{Cr}_2\text{O}_3$  together with the grain sizes at the mixed-oxide - pure-oxide interfaces are given in table II. All three oxide additions enhanced grain growth of the pure oxide at the interface, but only  $\text{MoO}_3$  and  $\text{WO}_3$  enhanced grain growth in the mixture. No correction was applied to the measured grain size in the mixtures for the area occupied by the addition because the added oxide either dissolved in the matrix or evaporated.

The second experiment was designed to determine whether Cr could diffuse into  $\text{MgO}$  to any measurable extent under the heat-treating conditions used for cermets in this investigation, since the interface effect may be caused by the metal instead of its oxide. A flat piece of electrolytic Cr was ground on both sides to a thickness of about 0.015 inch, placed on top of a ground specimen of hydrogen-cleaned and hot-pressed  $\text{MgO}$ , loaded in a tungsten boat, and then heat-treated at  $1605^{\circ}\pm 25^{\circ}$  C for 16 hours in an induction-heated vacuum furnace under a vacuum better than  $10^{-4}$  torr. The Cr had evaporated completely and the  $\text{MgO}$  specimen was green on all surfaces (see fig. 8). The  $\text{MgO}$  specimen was cut in half, showing that the green coloration reached to a depth of about 0.03 inch. X-ray diffraction analysis showed that the surface layer was  $\text{Cr}_2\text{O}_3$ - $\text{MgO}$  spinel and the inner layer a solid solution of  $\text{Cr}_2\text{O}_3$  in  $\text{MgO}$ .

## DISCUSSION OF RESULTS

Following Zener's analysis, Smith (ref. 3) has shown that the effect of inclusions (and perhaps pores) on grain size is given by the equation

$$D_f = \frac{3d}{4F} \quad (1)$$

where  $D_f$  is the limiting average grain size,  $d$  is the average diameter of the inclusion (or pore), and  $F$  is the volume fraction of inclusions. As shown by the results of the present investigation, at sufficiently large amounts of metal additions the grain size of  $\text{MgO}$  decreases (at a diminishing rate) as the amount of metal addition increases. Thus, at least qualitatively, this effect is as predicted by theory.

No attempt has been made to study the effect of pores on grain growth but the exper-

imental procedures used in this investigation were designed to keep the porosity at a constant low level. In addition, up to about 19 volume percent, porosity seems to have negligible effects on the grain growth of MgO (ref. 13), which was one of the reasons for having used this material for investigation.

As shown by equation (1), the ultimate grain size also depends on the diameter  $d$  of the inclusion. It can be surmised from this that the difference in grain sizes due to type of addition used may be due in part to the effect of particle size of the addition. It should be pointed out that the final diameter of the inclusions is not necessarily that of the original metal inclusion, as figure 1 (p. 4) shows. Although the importance of the particle size of the addition is clearly recognized, a detailed examination of this variable was beyond the scope of this investigation.

From examination of figures 3 to 5, it follows that the effectiveness of additions in excess of about 4 volume percent in inhibiting grain growth in MgO for 1 hour exposure at 1620° C decreases in the order Cr, Mo, W. Considering that the original particle sizes of Cr, Mo, and W are 0.52, 0.19, and 0.24, respectively, (table I, p. 2), it can be surmised that the effectiveness of a metal as a grain-growth inhibitor depends on other factors (including stability of inclusion particle size) in addition to original particle size.

Other factors besides inclusions (and pores) can affect grain growth, as indicated by Burke and Turnbull (ref. 2) who obtain for the time dependence of grain size,

$$D^2 - D_0^2 = K\rho Vt \quad (2)$$

where  $D$  is the grain size at time  $t$ ,  $D_0$  is the grain size at time  $t = 0$ ,  $K$  is a constant,  $\rho$  is the grain-boundary energy, and  $V$  is the atomic volume. If  $D_0^2$  is negligible compared with  $D^2$ , equation (2) simplifies to

$$D = (K\rho Vt)^{1/2} \quad (3)$$

Thus, under given heat-treating conditions, the grain size depends on the grain-boundary energy, which, in turn, can be expected to be affected by the presence of solutes in the matrix oxide. There are no data available on the effects of solutes on the grain-boundary energy of MgO, but it can be surmised that some solutes will increase and others decrease the grain-boundary energy, depending on the kind of addition and on its concentration at the grain boundary.

The two effects (grain-growth inhibition by impingement of the grain boundary with inclusions and changes in grain-boundary energy due to solutes from the addition) discussed previously could explain the maximums in some of the curves in figures 2 and 3 (p. 5) and the relatively flat portion of the curve in figure 4 (p. 6) (up to about 3-volume-percent Mo). Thus, at low-volume-percent addition, the number of inclusions may be

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insufficient to counteract the grain-growth enhancement due to solution of the addition in the matrix (or concentration of solute at the grain boundaries, as the case may be) and the grain-growth enhancement occurs. Eventually, at sufficiently large-volume-percent addition, the matrix (or the grain boundaries) may become saturated with solute, and the inclusions may become more and more effective in inhibiting grain growth. In addition, once the solubility limit of ions from the addition is exceeded, the resulting oxide may also contribute to grain-growth inhibition. The process is further complicated by the presence of metal from the matrix oxide, which results from the displacement reaction. This interpretation is substantiated by the results of experiments made in an effort to explain the maximums in the curves in figure 2 obtained at the beginning of this investigation.

As comparison of figures 2 and 3 will show, the hydrogen treatment causes the suppression of the maximum in the curve for  $1620^{\circ}\text{C}$ , indicating that the maximums may be due in part to the presence of reducible oxides. It is for this reason that, after the first set of curves (fig. 2) was obtained, all subsequent runs with cermets were of the hydrogen-cleaned and hot-pressed type because of the possible presence of oxides in the metal additions.

That foreign oxides can diffuse or evaporate (before the pores of the compact become discontinuous) into the oxide matrix is shown by the results of adding the oxides of W, Mo, and Cr to MgO. The results of these experiments are shown in table II. It is obvious that, in varying degrees, all three oxides enhance the grain growth of MgO. This grain-growth enhancement in the pure oxide is most pronounced at the interface where the concentration of the foreign oxide is highest. These results substantiate the theory regarding the presence of maximums previously postulated.

If an oxide can enhance grain growth, the metal itself should be able to do the same, since in either case ionic interaction is involved. To determine whether diffusion of a metal can account for the observed maximums, the experiment on the diffusion of Cr in MgO already described was carried out. This metal was chosen for the experiment because its green oxide is readily detectable in small concentrations. As shown in figure 8, diffusion of the Cr ion in MgO takes place readily. No attempt has been made to analyze grain-growth phenomena in this specimen because, at a given depth in the specimen, the grains grow first as in pure MgO, later grain growth would be enhanced by diffusion of the Cr ion, and still later grain growth may be inhibited by the phases resulting from the reaction (Mg metal and  $\text{MgO-Cr}_2\text{O}_3$  spinel).

It can be surmised from the results of these experiments that either the metal addition or its oxide can enhance grain growth by diffusion into the matrix oxide. The mechanism that is most important will depend on the amount of oxide contaminating the addition, the relative volatility of the addition and its oxide, and the volatility and effect of grain-growth inhibition (and/or enhancement) of reaction products (usually the metal or a

suboxide of the matrix oxide and the oxide of the addition). Thus, volatile oxides like those of W and Mo or volatile metals like Cr can evaporate readily at relatively low temperatures, coat the matrix-oxide particles before the pores become discontinuous and then either diffuse into the matrix oxide or form additional phases at the grain boundaries and thereby affect grain growth.

It is possible that some or all the preceding mechanisms (evaporation, oxide diffusion, metal diffusion, grain-growth inhibition by inclusions) are operative during the hot-pressing and heat-treating processes and that the curves for grain size against composition reflect the additive contribution of each effect, some of which may in turn be temperature and time dependent.

The effect of temperature on grain growth of MgO-W mixtures is shown in figure 6 (p. 7) where the data points from figures 2 and 3 (p. 5) have been replotted. As figure 6 shows, beyond about 4 volume-percent-tungsten addition at 1620° C, the grain size decreases with increasing volume percent of addition. At lower temperatures and/or volume percent addition, the deviation from this rule appears to be associated with the maximums in the curves for grain size against volume percent. The decrease in grain-growth rate due to the presence of sufficiently large amounts of inclusions was to be expected in view of the larger activation energy that would be required for the grain boundary to cut across inclusions.

The effects of time at temperature on the grain growth of MgO is shown in figure 7 (p. 7). Although equation (3) indicates that the grain size should increase as the square root of the time, experimental evidence for metals and alloys (ref. 2) and for oxides (ref. 14) shows considerable departure from the 1/2 power law. In general, these experimental data can be made to fit the equation proposed by Beck, et al. (ref. 15)

$$D = Kt^n \quad (4)$$

where  $n$  is the time exponent and  $K$  is a constant. Equation (4) is valid only for negligibly small initial grain size. In cases where the initial (i. e., as-hot-pressed) grain size is not negligible, Beck, et al. (ref. 15) suggest the equation

$$D = K(t + A)^n \quad (5)$$

where  $A$  is a constant.

Substitution of the data for MgO with 4-volume-percent tungsten in equation (5) yielded

$$D = 14(t + 2.5 \times 10^{-6})^{0.05} \quad (6)$$

The value of  $A$  is so small that for all practical purposes it can be neglected, and equation (5) reduces to the original equation (4). Taking logarithms of both sides of equation (4) yields

$$\log D = \log K + n \log t \quad (7)$$

where  $n$  can be determined readily from two data points. The approximate values of  $n$  shown in figure 7 were obtained from the first and last data points in each curve. An analysis of the data shown in figure 7 indicates that

(1) The value of  $n$  depends on the kind of addition and decreases in the order Cr, Mo, W.

(2) Additions of W, Mo, and perhaps Cr decrease  $n$  when the results are compared with those for pure MgO.

(3) The value of  $n$  is about the same for 4- and 8-volume-percent additions indicating that most of the decrease in  $n$  due to the addition occurs at volume percentages less than about 4.

## CONCLUDING REMARKS

It has been shown that additions of tungsten, molybdenum, and chromium in sufficiently large amounts (greater than about 4 volume percent) inhibit the grain growth of magnesium oxide at  $1620^{\circ}\text{C}$ . It would be expected that, as long as the metallic addition was compatible with the ceramic, the same phenomenon should occur with other ceramics. The theory for metals relating the effects of inclusions to grain growth appears to be valid for metal additions to ceramic oxides where the metal addition can be considered to act as an inclusion. At least qualitatively the effects of time at temperature on the grain growths were as predicted by theory.

The effectiveness of metallic additions as grain growth inhibitors, especially for oxide ceramics intended for high temperature usage, is apparently decreased by the presence of surface oxide films. This phenomenon can be minimized by reduction treatments before consolidation.

Relatively small amounts of foreign ions (from the addition, from the heat treating atmosphere, or already present in the matrix raw materials) can have a pronounced influence on grain growth. In some cases these foreign ions may actually accelerate grain growth.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, March 1, 1965.

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